

Aspen Plus[®] HDPE Production Process

Simulation of HDPE slurry phase reactor using Aspen Plus®



Compatible with Aspen Plus[®] v10 or Higher

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This document is developed to teach how to use the software. The document has gone
under several reviews to reduce any possible errors, though it may still have some. We
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Document history

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Rev 0	The first draft was prepared.	23-Nov-2020



Table of Contents

Title	Page
Problem Definition	4
Solution	4
New simulation	4
Component specification	5
Polymers characterization	5
Property model specification	7
Flowsheet development	9
FEED Stream	9
Reactor	10
Results	15
Sensitivity analysis	16
References	19
APPENDIX	19



Problem Definition

Consider a stream with the specified composition in Table 1 at pressure 200 KPa and temperature 358.15 K that enters the reactor as feed for the HDPE production process. The slurry phase reactor model is CSTR and operates at803.51 kPa. Volume of the reactor is 30.60 m³ and there is a thermodynamic equilibrium between the vapor and the slurry phase. Simulate the reactor and calculate the molecular mass distribution of the polymer (HDPE) in the reactor exit.

biezi nie valaes of the components involved in the protes						
Component	Mass flow rate [kg/hr]					
Titanium tetrachloride (Catalyst)	8.99					
Triethylaluminium (Co-catalyst)	8.99					
Ethylene (Monomer)	5999.70					
Hydrogen (Chain transfer agent)	0.3					
n-Hexane (Solvent)	53982					

Table1. The values of the components involved in the process

Note: You can find the simulation file this flowsheet online on <u>www.cemf.ir</u> alongside this tutorial file.

Solution New simulation

1. Start a new Aspen Plus[®] simulation with **Polymers with Met_C bar_hr Units** template.





Component specification

2. In the *Data Browser*, find **Component Specification** through root *Components/Specifications*, define include all the involved components in the simulation. The component ID is what you see in your input and output sheets of the software. So, you can change these IDs as shown below. Also select **polymer** and **segment** as type for **HDPE** and **C2H4-R**, respectively.

Hint!

 C_2H_4 -R refers to the undeveloped polymer chain at the end of which is a vacant site for reaction and allows the monomer to bind and the polymer chain to propagate.

ns 💌	Selection	Petroleum	Nonconventional	Senterprise Databas	e Comments		
Setup Components	Select compon	ents					
Specifications	Compo	nent ID	Тур	e	Compone	nt name	Alias
Assay/Blend	TICL4	C	onventional		TITANIUM-TETRA	ACHLORIDE	TICL4
💿 Light End Properties	TEA	C	onventional		TRIETHYL-ALUM	INUM	C6H15AL
Petro Characterization	C2H4-R	s	egment		ETHYLENE-R		C2H4-R
Component Attributes	C2H4	C	onventional		ETHYLENE		C2H4
📜 Henry Comps	HEXAN		onventional		N-HEXANE		C6H14-1
UNIFAC Groups Delument	H2	c	onventional		HYDROGEN		H2
Methods	HDPE	P	olymer		HIGH-DENSITY-P	OLY(ETHYLE	HDPE
Chemistry							
Property Sets	Co.d	C Flore 100			ad Deceder	Deview	٦
Data Estimation	Find	Elec W	IZard SFE Assis	User Defin	ed Keorder	Keview	
Analysis		2					
Customize							
Results							

Polymers characterization

3-1. In the *Data Browser*, find **Polymers-characterization** through root *Components/Polymers/Characterization*. In the **Segment** tab, select **C2H4-R** as the **Repeat** unit. Use this sheet to specify the type of all polymer and oligomer segments. Segments are the building blocks that participate in the polymer or oligomer chain. Segments can be repeated units, end groups, or branch points attached to three or four branches.

3-2. In **Polymers** tab, select the properties or component attributes that Aspen should tracked for the produced polymers. Component attributes keep track of polymer properties such as degree of polymerization, molecular weight, copolymer composition, etc. To do this, select the **Ziegler-Nata Selection** in the **Built-in attributes group** section. You will see a list of catalyst attributes below it. Site based component attributes are also available to simulate multi-site type Ziegler-Natta catalyst





polymerization. Composite attributes are summed over all site types. They represent the average properties of the polymer.



All Items 🔹	Segments	Polymers	Oligomers 🛛 🤇	Site-Based Species	Options	Comment
Components	Polymer ID	IDPE	-			
Assay/Blend Ight End Properties Petro Characterization	Built-in attrib	ute group Zie	gler-Natta sele	ction		> 5
Pseudocomponents	- Attribute list -					
Component Attributes	SFRAC	SFLOW	DPN	DPW	PDI	
🛅 Henry Comps	MWN	MWW	ZMOM	FMOM	SMOM	
🕝 UNIFAC Groups	LDPN	LZMOM	LFMOM	LSFLOW	LSFRAC	
A 🔯 Polymers	LEFLOW	LEFRAC	LPFRAC	SSFRAC	SSFLOW	
Characterization	SDPN	SDPW	SPDI	SMWN	SMWW	
Oistributions	SZMOM	SEMOM	SSMOM	SPFRAC	LSDPN	
Methods	LSZMOM	LSFMOM	LSSFLOW	LSSFRAC	LSEFLOW	-
Chemistry Chemistry	LSEFRAC	LSPFRAC				
Data						-
Estimation						Edit
🗀 Analysis						Luit
🗀 Customize						
🗀 Results						



3-3. In **Site-Based Species** tab, specify the structure and activity of site-based catalytic species such as coordination catalysts and ionic initiators. Polymerization reactions such as Ziegler-Natta polymerization and Ionic polymerization use multi-site catalytic species. Each site is responsible for producing polymer chains with different characteristics. Specify the number of site types in the Number of sites for the catalyst. You must also specify the moles of sites per gram of catalyst (as shown in the figure below).

Il Items 🔹	Segments Polymers Oligo	mers Site-Based Species Options Comments
Image: Second Structure Image: Second Structure Image: Second Structure Image: Second Structure	Site-based component © Ziegler-Natta catalyst Specifications Component ID Component	Ionic initiator 1
Light End Properties Petro Characterization Pseudocomponents	Number of site types	CPSFLOW CPSFRAC CDSFLOW CDSFRAC CISFLOW CISFRAC
 Henry Comps UNIFAC Groups O Characterization O Istributions Methods Chemistry Property Sets Data 	Max. sites: 0.00038 (site conc.)	3 4 Edit
Analysis		

Hint!

Component attributes are used to track multi-site heterogeneous polymerization (Ziegler-Natta) catalyst site activity, in terms of mole flow and the fraction of potential, inhibited, vacant, and dead sites. The occupied sites are not tracked since that information may be obtained from the live polymer zeroth moment of chain length distribution.

Property model specification

4-1. In the *Data Browser*, find **Properties Specification** through root *Properties/Methods/Specification* form. In **Global** tab, Select **PC-SAFT** as the base method and in **Referenced** tab, add **PC-SAFT** as the Referenced methods from Available methods list.

4-2. The PC-SAFT parameters for components $TiCl_4$ and TEA are not available in the data bank. You need to define the required scalar parameters of these components. Go to *Properties/Methods/Parameters/Pure Components,* add a **New** pure component scalar parameter (name it "PC-SAFT") and enter the values of each parameter according to what is shown in the figure. Then click next button ($N \rightarrow$) to review the binary interactions for this EOS.



Properties	Methods - Specifications × + 3
All Items	OGlobal Flowsheet Sections OReferenced Comments
 Estup Components 	Property methods & options Method name
🔺 🔯 Methods	Method filter POLYMER PC-SAFT Methods Assistant.
Specifications	Base method PC-SAFT
 Delected Methods Delected Methods Delected Methods 	Henry components 2 EOS ESPSAFT
📜 Routes	Petroleum calculation options
ONC Props	Weter colubility 2
Tabpoly	Data set
Property Sets	Electrolyte calculation options
Data	Chemistry ID
Estimation	Vise true components
analysis	
Customize	
- Reduc	Sendula referice state entitalpy
Properties	Methods - Specifications × +
All Items	Global Flowsheet Sections @Referenced Comments
 Setup Components Methods Specifications Selected Methods Selected Methods Routes NC Props 	Property methods for blocks and analysis Available methods Referenced methods NRTL-RK PC-SAFT NRTLSAC OLI PENG-ROB
Tabpoly	PITZ-HG
Chemistry	
Property Sets	



File	Home	View		Suston	nize	R	esources												
Cut Copy Paste Clipboard	☆ Cut METCBARF → ☞ Setup ☞ Copy ☞ Unit Sets ☞ Compo ☞ Paste Units ▲ Method						Chemistry Customize Prop Sets	Draw Structure		Methods Assi Clean Parame Retrieve Parar Tools	stant ters neters	Det NIST	IEMA	Analys Estima Regres Run Mo	ation asion ode	Next	Run	Reset	Control Panel
Propertie	5		<	F	Pure	Comp	onents - P	C-SAFT ×	+							31			
All Items					Ø In	put	Comment	ts											
🕨 🔯 Seti	up				Dure	com	nonent cca	lar paramet	orr				_		_		-		
 Cor Met Met 	mponents thods Specificatio	ins				Pa	rameters	Units	5	Data set	Con	nponent 4 -	Con TEA	nponent +	Com	nponent	-		
	Selected Me Parameters	ethods	-	11	1	PCS	FTM			1		30		30					
40	👸 Pure Co	mponer	nts		P.	PCS	FTU	к		1		236.77		236.77					
	PC-S	AFT			P.	PCS	FTV			1		3.7683		3.7683					
P L	Binary in	te Pair	m		×														
	 Electroly UNIFAC UNIFAC Results Routes NC Props Tabpoly emistry perty Sets a mation slysis ttomize ults 	rte Terna Groups Groups	Binary								2								

Flowsheet development FEED Stream

5. From **Module Palette**, drag a material stream into the **Main flowsheet window** and rename it (using Ctrl+M) to **FEED**. Double click on this stream to open stream specification form. Complete the feed condition as shown here.



6. In the **Components Attributes** section, enter the following values for each of the catalyst attributes:



Table2. Th	e values of the	compon	ents Att	ributes [1]
	Attributes ID	Value	Unit	
	CPSFLOW	1	[mol]	
	CPSFRAC	1	[-]	
	CVSFLOW	0	[mol]	
	CVSFRAC	0	[-]	
	CISFLOW	0	[mol]	
	CISFRAC	0	[-]	
	CDSFLOW	0	[mol]	
	CDSFRAC	0	[-]	

Co	mponent ID	OTICI	L 4	•
Att	ribute ID	V CPS	FLOW	•
	Eleme	nt	Value	
	CPSFLOW			1

Component attributes are used to track multi-site heterogeneous polymerization (Ziegler-Natta) catalyst site activity, in terms of mole flow and fraction of potential, inhibited, vacant, and dead sites. The site types are defined as follows:

Note

- Potential Sites sites that are not yet activated.
- Vacant Site sites that are activated without a growing polymer attached.
- Inhibited Sites activated sites that are temporarily in inactive state.
- Dead Sites sites that have permanently lost their catalytic activity.
- Occupied Sites activated sites with a growing polymer attached.

Reactor

7. From **Module Palette, Reactor** tab, drag a **RCSTR** and connect the FEED stream to its inlet port. Drag two material streams into the flowsheet and connect them to the **Product** ports (one as the slurry phase outlet stream and the other as the vapor phase outlet stream). Rename them to **LIQPROD** & **VAPPROD**, as shown:

Model Palette							
R	Mixers/Splitters	Separators	Exchangers	Columns	Reactors	Pressure Changers	Manipulators
→ → Material	RStoic -	RYield -	REquil -	RGibbs	- CSTR	• RPlug	RBatch





Hint! To connect the **FEED** stream to the **CSTR**, right-click on **FEED** and select the **Reconnect Destination** to set the stream destination to the reactor inlet.



8. Double click on the **CSTR** to open the reactor specification form. Complete the operating conditions and output stream phases here. In **Specifications** tab, select **Vapor-liquid** mode as the **Valid phases** and enter the value **0.1** for the **volume fraction** of the vapor phase. Then, in **Streams** tab select liquid and vapor phase for **LIQPROD** and **VAPPROD**, respectively.



Temperature Duty		803.51 358.15	kPa K kcal/br	-					
Vapor fractio	n		Kudiy III			2			
oldup ———	-				-	3	Ì		
id phases ecification tyj	Vapor-Liquid Reactor volum	ne & Phase volu	me fractior	• • •		Liquid			
Reactor		Pha	se				1		
/olume	30600 I	▼ Pha	se	Vapor phase		-			
lesi. tim	hr	Vol	lme		1				
	7	Vol	ume frac			0.1			
		Res	idence time		hr	*			
					-	5			
						1	5		



9. In **Reactions** tab, click **New** button and enter R-1 for this new reaction set. Then, Select **ZIGLER-NAT** from the menu and then move **R-1** to **Selected Reaction Sets**.



Select reaction sets to be included in the model Available reaction sets Selected reaction sets Selected reaction sets C.Click here Reaction Set C.Click here Selected reaction Set Select reaction sets Selected reaction sets Select reaction	Select reaction sets to be included in the model Available reaction sets Selected reaction sets Selected reaction sets Color Cancel Col	Specifications	Streams	Reactions	PSD	Component Attr.	Utility	Catalyst	Comments	
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Available reaction sets R-1 5 >>> >>> >>> New Name Value	Available reaction sets R-1 5 >>> >>>	- Select reaction se	ts to be include	d in the model		_				
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		Value								

10-1. In the *Data Browser*, Go to *Reactions/R-1*, and fill in the blanks in **Species** tab with the proper values as shown below.

 Setup Property Sets 	Species	Reactions	Rate Constants	Options	Comments		
Property Sets 2 Analysis 2 Analysis 2 Convergence 2 Convergence 2 Dec LOPROD Convergence 2 Dec CTR Convergence 2 Dec Options Dec Dec Options Dec	Polymer HDPE Monomers goes to -> Precatalyst Catalysts Cocatalysts Solvents Transfer ag. Hydrogens Poisons Electr. don. Byproduct	C2H4 C2H4-R TICL4 HEXAN HEXAN	• T.D.	3. sigment	3		



10-2. In **Reactions** tab, click on **Generate Reactions** button. Then, remove the reactions that are not listed in Table 3.

					. consta	1113 [2]	
Reaction Name	Reaction Types	Reactants	Site1	Site2	Site3	Site4	Unit
Spontaneous activation	ACT-SPON	Cps[TiCl ₄]	186.9	370.2	128.38	497.97	[L/mol.s]
Chain initiation	CHAIN-INI	Ро	456.3	1.686	0.655	4.05	[L/mol.s]
Propagation	PROPAGATION	$Pn[C_2H_4] + C_2H_4$	240	270	310	16	[L/mol.s]
Chain transfer to monomer	CHAT-MON	$Pn[C_2h_4] + C_2h_4$	0.986	0.303	0.27	0.005	[L/mol.s]
Chain transfer to hydrogen	CHAT-H2	$Pn[C_2h_4] + H_2$	5.55	18.5	0.002	2.7e-06	[L/mol.s]
Chain transfer to Spontaneous	CHAT-SPON	Pn[C ₂ h ₄]	0.002	0.001	0.00035	8.7e-10	[L/mol.s]
Spontaneous deactivation	DEACT-SPON	Po/Pn	0.002	0.00098	0.00034	0	[L/mol.s]

Table 3. Literature Data of Pre-Exponential Kinetic Rate Constants [2]

* The order of chain transfer to hydrogen was considered one instead of the original value of 0.5 in the reference.

Generate Reactions	2.Click here					
New Edit Reaction	Edit Rate Constants					
Reaction	Reactants		Products	Active	Delete	A
1) Act-Spon (1)	Cps[Ticl4]	->	Po	V	×	
2) Act-Spon (2)	Cps[Ticl4]	->	Po	V	×	
3) Act-Spon (3)	Cps[Ticl4]	->	Po		×	
4) Act-Spon (4)	Cps[Ticl4]	->	Po	V	×	-
5) Chain-Ini (1)	Po	->	P1[C2h4-R]		×	
6) Chain-Ini (2)	Po	->	P1[C2h4-R]	V	×	
7) Chain-Ini (3)	Po	->	P1[C2h4-R]	V	×	
8) Chain-Ini (4)	Po	->	P1[C2h4-R]	V	×	
9) Propagation (1)	Pn[C2H4] + C2H4	->	Pn+1[C2h4]	V	×	
10) Propagation (2)	Pn[C2H4] + C2H4	->	Pn+1[C2h4]	V	×	
11) Propagation (3)	Pn[C2H4] + C2H4	->	Pn+1[C2h4]		×	
12) Propagation (4)	Pn[C2H4] + C2H4	->	Pn+1[C2h4]		×	
13) Chat-Mon (1)	Pn[C2h4] + C2h4	->	Dn + P1[C2h4]	V	×	
14) Chat-Mon (2)	Pn[C2h4] + C2h4	->	Dn + P1[C2h4]		×	
15) Chat-Mon (3)	Pn[C2h4] + C2h4	->	Dn + P1[C2h4]	V	×	

10-3. In **Rate Constant** tab, Enter the values in **Pre-Exp** column using Table 3. Set the unit of these values to **1/sec**.



					2.Enter Pr	e-Exp valu	ies from [lable3
Туре	Site No.	Comp 1	Comp 2	Pre-Exp	Act-Energy	Order	Tdb Frac	Ref. Temp.
				1/sec 🔹	J/kmol -			с -
ACT-SPON	1	TICL4		186.9	0	1		1e+35
ACT-SPON	2	TICL4		370.2	0	1		1e+35
ACT-SPON	3	TICL4		128.38	0	1		1e+35
ACT-SPON	4	TICL4		497.97	0	1		1e+35
CHAIN-INI	1	C2H4		1.686	0	1		1e+35
CHAIN-INI	2	C2H4		0.655	0	1		1e+35
CHAIN-INI	3	C2H4		4.05	0	1		1e+35
CHAIN-INI	4	C2H4		0.204	0	1		1e+35
PROPAGATION	1	C2H4	C2H4	240	0	1		1e+35
PROPAGATION	2	C2H4	C2H4	270	0	1		1e+35
PROPAGATION	3	C2H4	C2H4	310	0	1		1e+35
PROPAGATION	4	C2H4	C2H4	16	0	1		1e+35
CHAT-MON	1	C2H4	C2H4	0.986	0	1		1e+35
CHAT-MON	2	C2H4	C2H4	0.303	0	1		1e+35
CHAT-MON	3	C2H4	C2H4	0.27	0	1		1e+35
CHAT-MON	4	C2H4	C2H4	0.005	0	1		1e+35
CHAT-H2	1	C2H4	H2	5.5	0	1		1e+35
CHAT-H2	2	C2H4	H2	18.5	0	1		1e+35

11. Click **Run** button (**>**) from **Home** tab or press **F5** to run the simulation. Then Double click on the **CSTR** block to see the results. From the top ribbon, in the **plot** section, select the **Chain Size Distribution** to plot the size distribution of each site and combined sites.



Results



12. Check the **Select All** to show the molecular weight distribution and chain size distribution of all active sites.

🔊 Chain Size Distr.		-3	×
Composite			
Show average prop	perties		
Select all	Check this.		
Site2			
🔽 Site3			
✓ Site4			
	OK Cancel		
	OK Cancel		

13. In the design tab, select **Molecular weight distribution (MWD)** to plot data.





The above figure shows the normalized molecular weight distribution (MWD) for HDPE polymer **CSTR**, in the outlet stream based on two calculation methods for average molecular properties: instantaneous distribution and moments of distribution. Notice that MWW = MWN × PDI. For more information on molecular weight distribution properties, see **APPENDIX**.

Sensitivity analysis



A sensitivity analysis was carried out to see the effect of H_2 flow rate in the **FEED** stream on the HDPE polymer properties such as MWN and MWW. The following figure, shows **Vary** and **Define** tab setup form of the sensitivity analysis tool in Aspen. The mass flow rate of H_2 is varied from 0 to 1 kg/h. **MWW** and **MWN** are defined as **Compattr-Var** in **LIQPROD** stream (you can find sensitivity analysis tool in path *Data Browser/Model analysis tool/Sensitivity*).

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The following two figures show the variations of **MWN** and **MWW** as functions of H_2 flow rate in the **FEED** stream. Notice that both MWN and MWW decrease as H_2 flow rate is increased, indicating that



 H_2 competes with the propagation of repeat unit $\mathsf{C}_2\mathsf{H}_4$ and prematurely terminates active site propagation.









References

[1] K. Al-Malah, *Aspen plus*, 1st ed. USA: John Wiley & Sons, Inc., 2016, pp. 325-360. Available: 10.1002/aic.14527 [Accessed 22 November 2020].

[2] C. Zhang, Z. Shao, X. Chen, Z. Yao, X. Gu and L. Biegler, "Kinetic parameter estimation of HDPE slurry process from molecular weight distribution: Estimability analysis and multistep methodology", *AIChE Journal*, vol. 60, no. 10, pp. 3442-3459, 2014. Available: 10.1002/aic.14527 [Accessed 22 November 2020].

APPENDIX

The number average molecular weight (MWN) and weight average molecular weight (MWW)

The average properties of the polymer chain can be calculated as ratios of the moments. The numberaverage degree of polymerization (DPN) is the ratio of the first to the zeroth moments, λ_1/λ_0 . On the other hand, the weight-average degree of polymerization (DPW) is the ratio of the second to the first moments, λ_2/λ_1 . In general, for a polymer with a chain length distribution, the nth moment is given by:

$$\lambda_m = \sum_{n=1}^N n^m Q_n$$

where

λ Moment

- m Moment order
- n Chain length or degree of polymerization
- Q_n Number of moles of polymer of length n

The polymer average chain length and weight properties are then calculated as follows:

A-1



A-6

DPN=Number-Average degree of polymerization= $\frac{\lambda_1}{\lambda_0} = \frac{FMOM}{ZMOM}$	A-2
DPW=Weight-Average degree of polymerization= $\frac{\lambda_2}{\lambda_1} = \frac{SMOM}{FMOM}$	A-3
PDI=Poly dispersity index= $\frac{DPW}{DPN} = \frac{\left(\frac{\lambda_2}{\lambda_1}\right)}{\left(\frac{\lambda_1}{\lambda_0}\right)} = \frac{(\lambda_2 \times \lambda_0)}{(\lambda_1)^2} = \frac{(SMOM \times ZMOM)}{(FMOM)^2}$	A-4
MWN=Number-Average molecular weight= $DPN \times \overline{M}_{segment}$	A-5

MWW=Weight-Average molecular weight= $DPW \times \overline{M}_{segment}$